

# REPORT DOCUMENTATION PAGE

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13. ABSTRACT (Maximum 200 Words)  We have made considerable advances in the development of optical-limiting systems based upon two-photon absorption processes. To accomplish this, it has been essential to develop an understanding of basic structure-property relationships for conjugated organic materials. To this end, we have investigated a range of phenylene-vinylene-based materials substituted with various combinations of donor and acceptor moieties. We now have a more thorough understanding of how to design materials with very high two-photon cross-sections in any part of the visible spectrum, opening the possibility for broad-band optical limiting based on a combination of these materials. We have used the dioxaborine moiety as an acceptor in a variety of conjugated systems and have found that in certain molecular architectures, this can lead to very high two-photon cross-sections. Some of the dioxaborine moieties also show very high electron mobilities, suggesting applications as charge carriers in photorefractive polymer composites. New carbazole-based materials have been designed and synthesized and are anticipated to be more photostable than related bis(diarylamo) biphenyls, whilst retaining the charge carrying and optical-limiting properties of the latter class of materials. Finally, the charge-transporting and optical-limiting bis(diarylamo) biphenyl group has been incorporated into new polymers, that can readily be cast into thermally stable films.			
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## 2. *Objectives*

The objectives of this work are to develop materials for: 1) protection of eyes and sensors from intense laser pulses and 2) for efficient photorefractive polymers.

## 3. *Status of effort*

We have made considerable advances in the development of optical-limiting systems based upon two-photon absorption processes. To accomplish this, it has been essential to develop an understanding of basic structure-property relationships for conjugated organic materials. To this end, we have investigated a range of phenylene-vinylene-based materials substituted with various combinations of donor and acceptor moieties. We now have a more thorough understanding of how to design materials with very high two-photon cross-sections in any part of the visible spectrum, opening the possibility for broad-band optical limiting based on a combination of these materials. We have used the dioxaborine moiety as an acceptor in a variety of conjugated systems and have found that in certain molecular architectures, this can lead to very high two-photon cross-sections. Some of the dioxaborine moieties also show very high electron mobilities, suggesting applications as charge carriers in photorefractive polymer composites. New carbazole-based materials have been designed and synthesized and are anticipated to be more photostable than related bis(diarylarnino)biphenyls, whilst retaining the charge carrying and optical-limiting properties of the latter class of materials. Finally, the charge-transporting and optical-limiting bis(diarylarnino)biphenyl group has been incorporated into new polymers, that can readily be cast into thermally stable films.

#### 4. Accomplishments and new findings

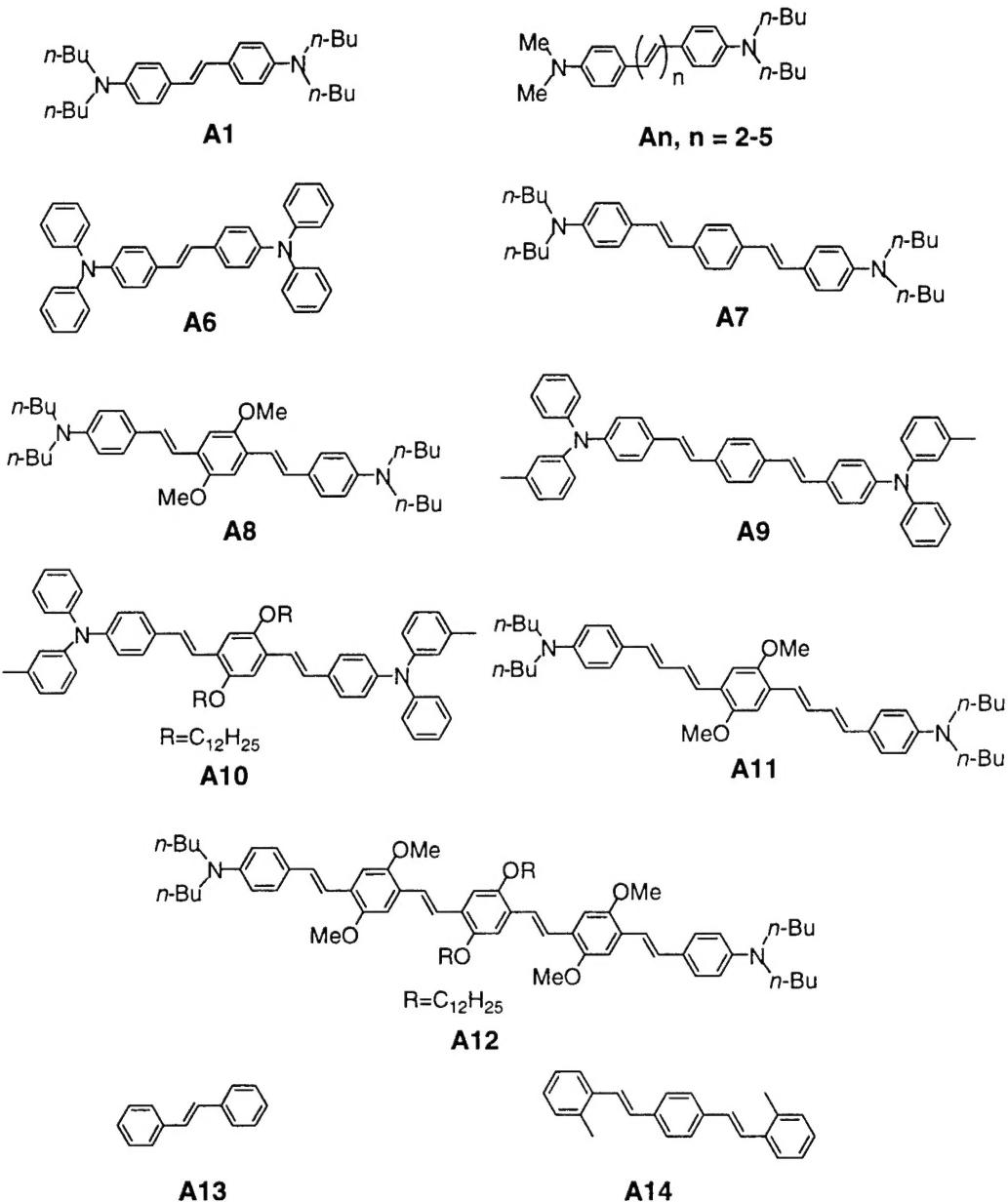
This section is divided into the following sections:

- 4A. Development of structure-property relationships for two-photon absorbing molecules based upon phenylene-vinylene motifs
- 4B. Development of structure-property relationships for two-photon absorbing molecules based upon the dioxaborine heterocycle motif
- 4C. Carbazole dimers for optical-limiting and photorefractive applications
- 4D. TPD polymers for optical-limiting and photorefractive applications

#### **4A. Development of structure-property relationships for two-photon absorbing molecules based upon phenylene-vinylene motifs (work done in collaboration with J. Perry and J.L. Brédas)**

Two-photon absorption provides a useful mechanism for optical limiting, especially when coupled with excited-state absorption subsequent to the two-photon process [Perry, J. W.; Barlow, S.; Ehrlich, J. E.; Heikal, A. A.; Hu, Z. Y.; Lee, I.-Y. S.; Mansour, K.; Marder, S. R.; Röckel, H.; Rumi, M.; Thayumanavan, S.; Wu, X. L. *Nonlinear Optics* **1999**, *21*, 225-243; Ehrlich, J. E.; Ananthavel, S. P.; Barlow, S.; Mansour, K.; Mohanalingam, K.; Marder, S. R.; Perry, J. W.; Rumi, M.; Thayumanavan, S. *Nonlinear Optics* **2001**, *27*, 121-131]. We have been developing a strategy for the design of centrosymmetric molecules with large two-photon absorption cross-sections,  $\delta$ . This strategy is based on the concept that symmetric charge transfer upon excitation, from the ends of a conjugated system to the middle, or *vice versa*, is correlated to enhanced values of  $\delta$ . Newly synthesized conjugated molecules with donor- $\pi$ -donor (D- $\pi$ -D), donor-acceptor-donor (D-A-D), acceptor- $\pi$ -acceptor (A- $\pi$ -A), and acceptor-donor-acceptor (A-D-A) structural motifs exhibit exceptionally large values of  $\delta$ , up to ~400 times that of *trans*-stilbene. Figure A1 shows the structures of some of the D- $\pi$ -D compounds we have synthesized and for which two-photon spectra have been recorded in

collaboration with Professor Joseph Perry's group at the University of Arizona, together with the structures of two references compounds without donor substituents (**A13** and **A14**).



**Figure A1.** Some molecules studied for two-photon absorption.

The origin of the large two-photon absorptivities in these molecules can be understood by considering the sum-over-states (SOS) expression for  $\delta$  derived from

perturbation theory. A simplified form of the SOS expression for the peak two-photon resonance value of  $\delta(\omega)$  for the  $S_0 \rightarrow S_2$  transition,  $\delta_{S_0 \rightarrow S_2}$ , is:

$$\delta_{S_0 \rightarrow S_2} \propto \frac{M_{01}^2 M_{12}^2}{(E_1 - E_0 - \hbar\omega)^2 \Gamma} \quad (1)$$

where the subscripts 0, 1, and 2 refer to  $S_0$ ,  $S_1$ , and  $S_2$  states,  $\omega = (E_2 - E_0) / 2$ , and  $\Gamma$  is the damping factor for the  $S_0 \rightarrow S_2$  transition. This expression results from taking  $S_1$  as the dominant intermediate state and is valid when  $(E_1 - E_0 - \omega)$  is large compared to the damping factor for the  $S_0 \rightarrow S_1$  transition. We conjectured that the large  $\delta$  observed in our chromophores were associated in large part with an enhancement of the transition moment  $M_{12}$  (also referred to as  $M_{ee'}$ ). To test this hypothesis we calculated  $M_{ee'}$ , using the simplified SOS expression and independent measurements of  $\delta$  (from the two-photon absorption spectra),  $M_{01}$  (also referred to as  $M_{ge}$ ) and  $(E_1 - E_0 - \omega)$  from the one-photon absorption spectra. The results shown in Table A2 indicate that, upon increasing the length of the molecules by inserting double bonds, the main increase in  $\delta$  derives from an increase in  $M_{ge}$ ; however, upon going from a stilbene to a bis(styryl)benzene, in accord with our expectation, there is also a significant increase in  $M_{ee'}$ . In fact, although not shown in Table A1, substitution of the central benzene ring of **A7** or **A9** with acceptors (in particular cyano groups) leads to a roughly 50% increase in  $M_{ee'}$ . These results substantiate our hypotheses outlined above.

**Table A1.** Position ( $\lambda_{max}^{(2)}$ , in nm) and magnitude ( $\delta_{max}$ , in  $10^{-50}$  cm<sup>4</sup> s/photon-molecule) of the peak two-photon absorption of bis(aminophenyl)polyenes from two-photon-induced fluorescence measurements using nanosecond and picosecond laser pulses, and from quantum-mechanical calculations (for simplified molecules with <sup>n</sup>Bu groups replaced with Me). The experimental uncertainty on  $\delta_{max}$  is of the order of 10-15% (25% for compound **A5**, due in part to the low fluorescence quantum yield).

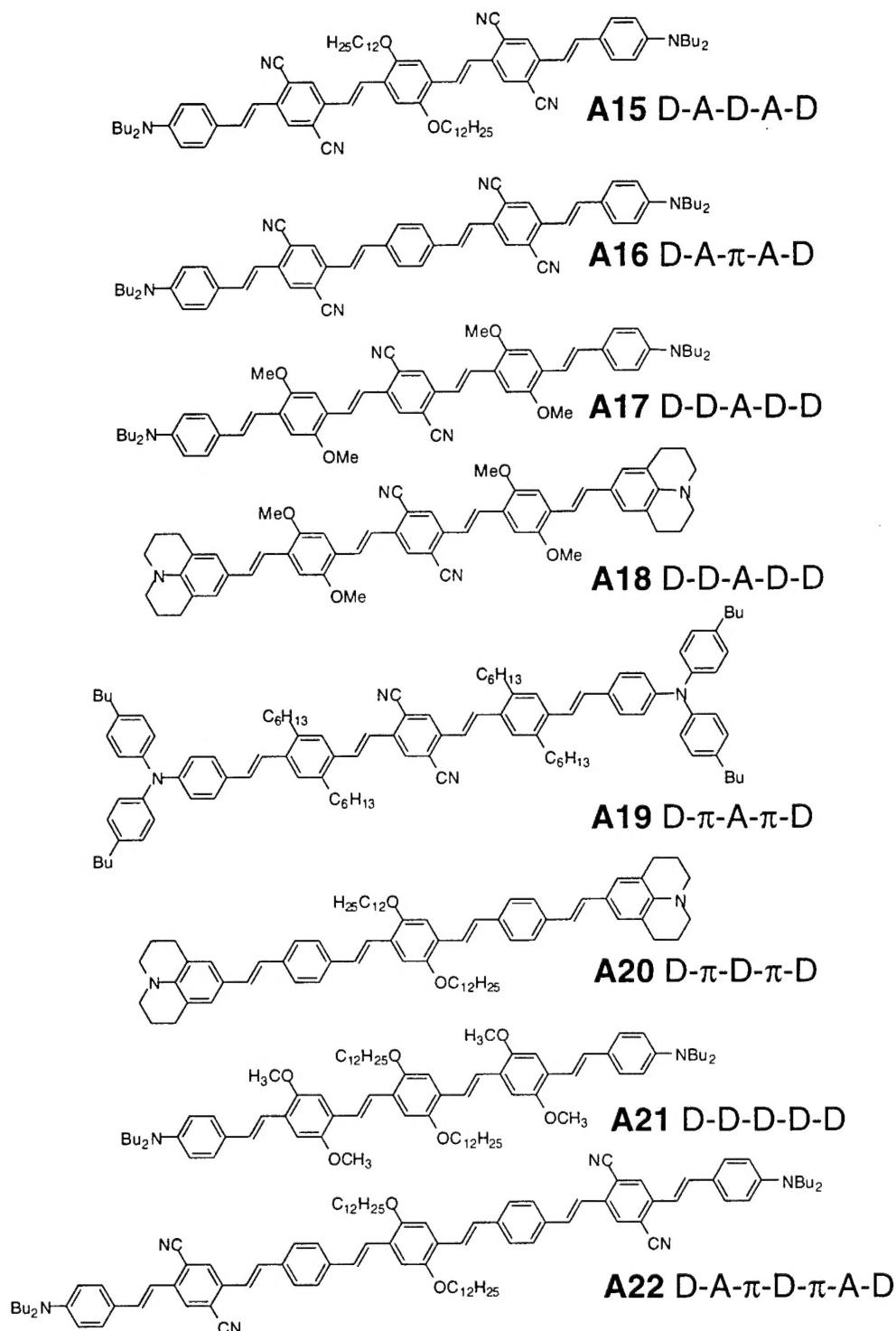
Compound	ns measurements		ps measurements		Compound	calculations	
	$\lambda_{max}^{(2)}$	$\delta_{max}$	$\lambda_{max}^{(2)}$	$\delta_{max}$		$\lambda_{max}^{(2)}$	$\delta_{max}$
<b>A1</b>	600	200	605	240	<b>A1'</b>	484	147
<b>A2</b>	640	260	640	230	<b>A2'</b>	519	195
<b>A3</b>	710	320	695	340	<b>A3'</b>	544	219
<b>A4</b>	730	425	695	410	<b>A4'</b>	564	227
<b>A5</b>	730	1300					
<b>A6</b>			690	190			

**Table A2.** Linear absorption maximum ( $\lambda_{max}^{(1)}$ ), extinction coefficient  $\epsilon_{ge}$  at  $\lambda_{max}^{(1)}$  ( $\epsilon_{max}$ ), transition dipole moment  $M_{ge}$ , detuning energy  $\Delta E = E_{ge} - 1/2E_{ge'}$ . ( $E_{ge}$  and  $E_{ge'}$  are the energies of the transitions  $g \rightarrow e$ , and  $g \rightarrow e'$ , respectively, derived from  $\lambda_{max}^{(1)}$  and  $\lambda_{max}^{(2)}$ ) and transition dipole moment  $M_{ee'}$ , for compounds **A1-A12** (Figure A1), **A13** (stilbene) and **A14** (1,4-bis(2-methylstyryl)benzene). The transition moments are expressed in Debye (D).

Compound	$\lambda_{max}^{(1)}$ (nm)	$\epsilon_{max}$ (M <sup>-1</sup> cm <sup>-1</sup> )	$M_{ge}$ (D)	Detuning energy (eV)	$M_{ee'}$ (D)
<b>A1</b>	374	46000	7.67	1.25	5.80
<b>A2</b>	390	65000	9.38	1.24	5.73
<b>A3</b>	412	81000	10.9	1.26	6.17
<b>A4</b>	430	96000	12.4	1.18	6.03
<b>A5</b>	449	103000	12.8	1.06	9.18
<b>A6</b>	387	47000	8.06	1.41	6.78
<b>A7</b>	409	74000	10.7	1.33	12.1
<b>A8</b>	429	67000	10.5	1.19	10.5
<b>A9</b>	411	63000	10.0	1.35	12.0
<b>A10</b>	426	65000	10.8	1.25	10.6
<b>A11</b>	454	93000	12.8	1.13	10.2
<b>A12</b>	468	110000	14.2	1.17	11.0
<b>A13</b>	297	31000	6.82	1.76	1.93
<b>A14</b>	350	50500	9.01	1.36	2.81

In an effort to further define the structure-property relationships for two-photon absorption, in order to learn how to develop new and improved materials for optical limiting applications, we have synthesized extended conjugated molecules (Figure A2) containing various permutations of donors (D), acceptors (A) and unsubstituted  $\pi$ -conjugated bridges

( $\pi$ ). We were interested in exploring whether increased length and different substitution patterns of donors and acceptors could be used effectively to control the magnitude and position of the peak of the two-photon absorption spectrum. Accordingly, the molecules in Figure A2 were synthesized through a series of multistep reaction sequences, making considerable use of the Wittig and Horner-Emmons reactions, in which aldehydes are reacted with deprotonated phosphonium salts and phosphonates respectively, to form the CH=CH linkages. For **A19** the phenylene vinylene linkages were made using the palladium-catalyzed Heck coupling of an aryl iodide and a vinyl group. Several related polymers have also been made using Heck chemistry. All compounds were characterized by NMR, UV-visible spectroscopy, electrochemistry, mass spectroscopy and elemental analysis. Table A3 summarizes some of the one-photon optical properties and the electrochemistry (from which the HOMO and LUMO energies can be estimated) for these species. Professor Joseph Perry's group is currently studying the two-photon fluorescence spectroscopy of these molecules, together with their use as optical limiting materials. For example, **A19** has been found to have good transparency in the range 600–900 nm, but with a very large two-photon cross-section in this region.



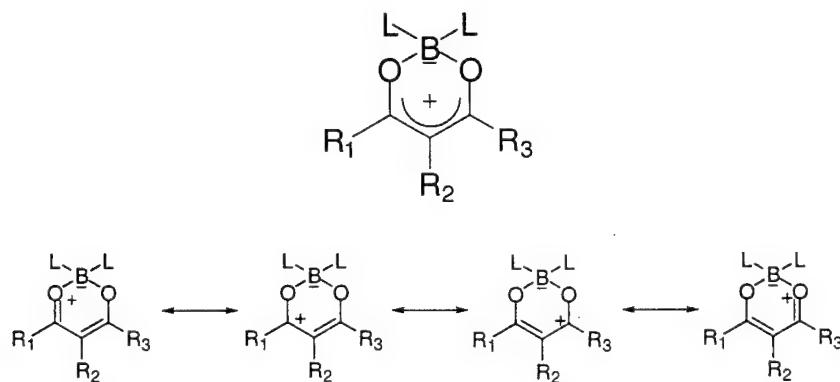
**Figure A2.** Extended phenylene-vinylene two-photon absorbing dyes.

**Table A3.** Spectroscopic and electrochemical measurements for the extended two-photon dyes as shown in Figure A2.

compound	$\lambda_{\text{max}}$ (absorption) / nm	$\lambda_{\text{max}}$ (emission) / nm	$E_{1/2}$ (oxidation) / mV	$E_{1/2}$ (reduction) / mV
<b>A15</b>	493	633	+322 (irrev.)	-1874
<b>A16</b>	489	636	-	-1822 (irrev.)
<b>A17</b>			+64	
<b>A19</b>			+309	-1854
<b>A20</b>	454	591	-67, +378	
<b>A21</b>	468	558	+67, +323	-
<b>A22</b>	463	608	+282	

**4B. Development of structure-property relationships for two-photon absorbing molecules based upon a doxaborine heterocycle motif (work done in collaboration with J. Perry and J.L. Brédas)**

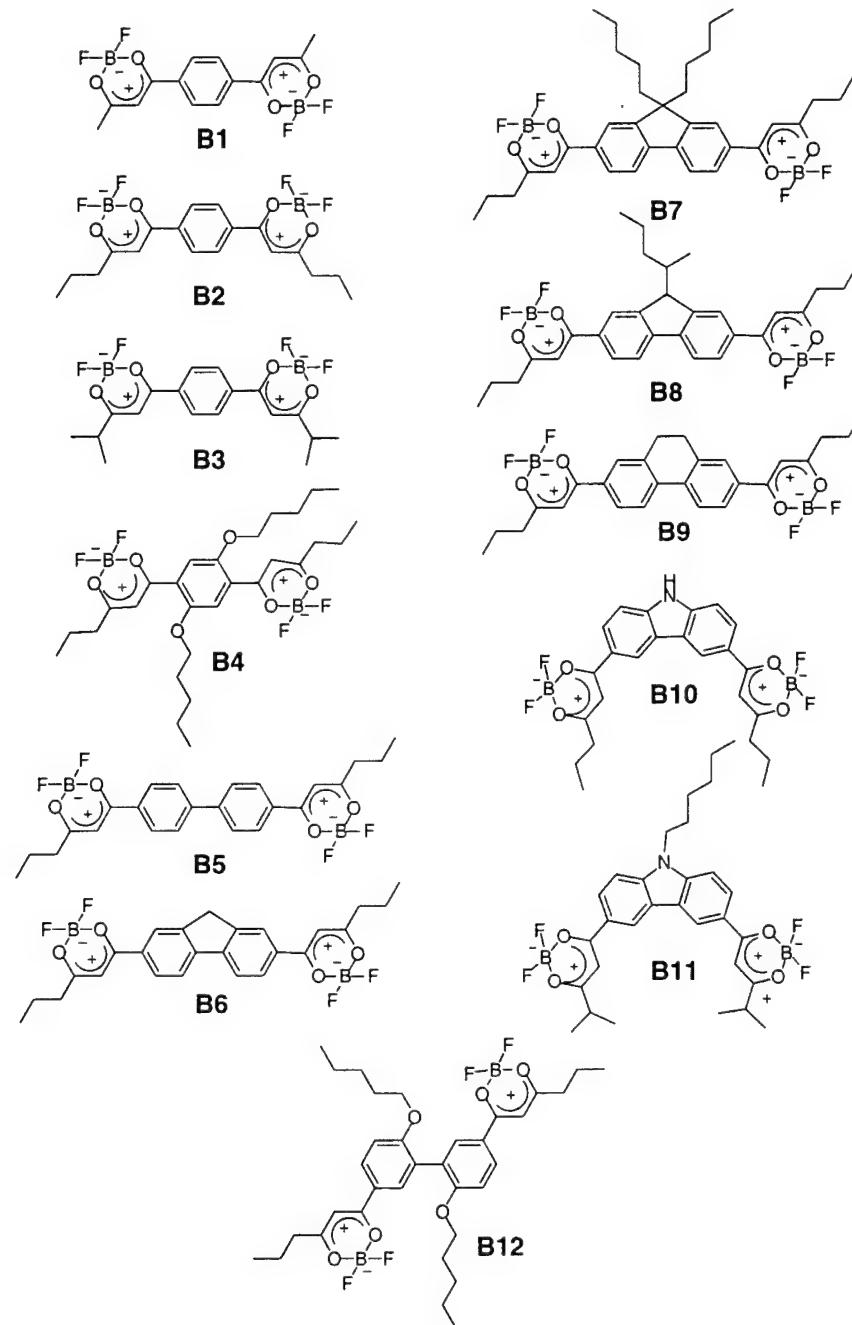
We have been exploring a new class of material called dioxaborines (DOBs); the general structure of the DOB moiety is shown in Figure B1. As indicated by the resonance structures in Figure B1, the boron atom fixes a negative charge so the  $\pi$ -system of the dicarbonyl ligands is positive charged. The DOBs have some remarkable properties: they are strong  $\pi$ -electron acceptors, are strongly absorbing, have high thermal stability and, in contrast to diketonate complexes with heavy metal ions, have strong fluorescence both in solution and in the solid state. We have exploited the acceptor properties of dioxaborine heterocycles to create new two-photon absorbing materials which may be useful for optical limiting, as charge-transfer systems for optical limiting (in combination with donor substituted systems), as two-photon absorbing sensitizers for photorefractive polymers, and as initiators for microfabrication applications. In addition, we have found that some DOB derivatives exhibit high electron mobilities, which points to potential application in photorefractive polymer composites.



**Figure B1.** General chemical structure and resonance forms for a dioxaborine.

As discussed in section 4A, conjugated molecules have been found to exhibit high two-photon cross-sections when acceptors (A), donors (D) and  $\pi$ -bridges ( $\pi$ ) are connected in certain sequences. We have therefore designed and synthesized a range of DOB derivative in

which the basic DOB building block acts as the acceptor (A) in the following molecular architectures: A- $\pi$ -A, A-D-A, and D-A-D. A few other species, not readily classified in this way, were also synthesized as model reference compounds.

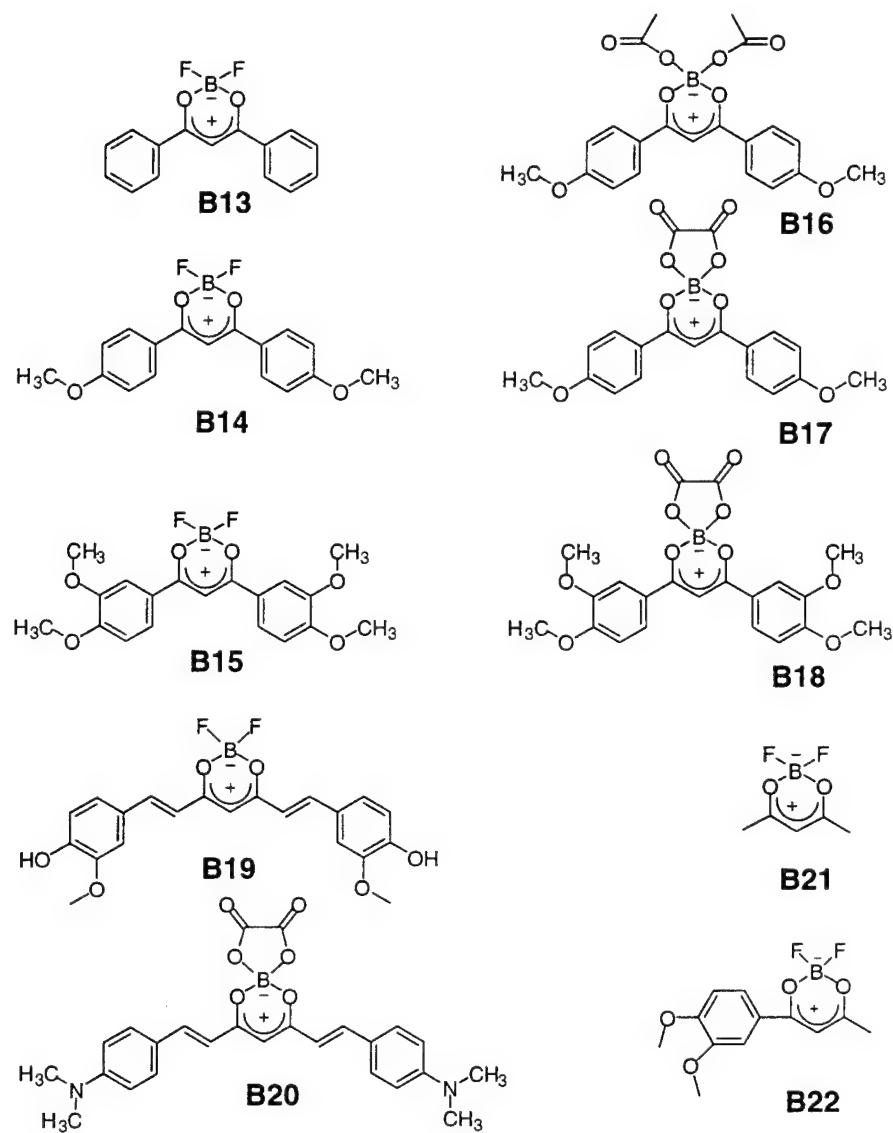


**Figure B2.** Structures of some bis(DOB)s with A- $\pi$ -A and A-D-A structural motifs.

Figure B2 shows the structures of a range of bis(DOB) derivatives. Compounds **B1-B4** are based upon the *p*-phenylene core; **B1-B3** are A- $\pi$ -A compounds, **B2** and **B3** being more soluble variants of **B1**, whilst **B4** has the A-D-A structural motif. **B5-B9** are A- $\pi$ -A with variants on the longer 4,4'-biphenylene bridge. **B10** and **B11** both have the nitrogen donor of the carbazole in conjugation with the DOB units and, so, are a type of A-D-A structure. The remaining structure, **B12**, based upon the 3,3'-biphenylene bridge, does not have direct conjugation between the two acceptor moieties and can be regarded as pairs of back-to-back D-A units.

Figure B3 shows some additional dioxaborines in which the DOB is the acceptor in a D-A-D system. In addition, the " $\pi$ -A- $\pi$ ", **B13**, the model non-conjugated DOB **B21**, and the D-A molecule **B22**, are shown.

The absorption spectra of the new DOBs were obtained; for some examples fluorescence quantum yields were also obtained (Table B1). The simple DOB **B21** – which has only two methyl groups on the dioxaborine ring – has the highest energy absorption (288 nm). The other data show the expected effects of conjugation. The fluorescence data are in agreement with the general tendency of DOBs to be highly fluorescent.



**Figure B3.** Some D-A-D dioxaborines and related model compounds.

Two-photon spectra of some of the DOBs have been measured using two-photon induced fluorescence for a range of DOB derivatives. The spectra are summarized in Table B2; the maxima in the two-photon spectra are followed by the strengths of these peaks, measured as the product of the two-photon cross-section,  $\delta$ , and the fluorescence quantum yield,  $\eta$ .

**Table B1.** Absorption maxima ( $\lambda_{\max}$ ) and fluorescence quantum yields ( $\eta$ ) for some DOBs in dichloromethane.

Compound	$\lambda_{\max}$ / nm	$\eta$
<b>B3</b>	367	
<b>B4</b>	354	0.55
<b>B11</b>	422	
<b>B12</b>	369	0.47
<b>B20</b>	499	
<b>B21</b>	288	
<b>B22</b>	375	0.70

In many of these spectra, there are two principal peaks. A weak low energy band is seen at approximately twice the wavelength of the one-photon maximum (for example, **B11** shows a one-photon maximum at 422 nm, whilst the lower energy two-photon peak is at 840 nm), and a higher energy stronger peak. This is a slightly more complex situation than that found for the compounds in section 4A. Although the low energy maximum roughly corresponds with that expected for two-photon excitation into the weakly allowed lowest energy one-photon excited state, calculations carried out in Jean-Luc Brédas' group suggests this is not the case. Further computational work is in progress to gain a fuller understanding of the complex two-photon spectroscopy of these species. Regardless of these complications, a general observation, important for optical limiting, is that the main two-photon peak of these compounds is always found in the region of the spectrum where one-photon absorption is negligible.

The  $\eta\delta$  values for simple DOBs, such as the " $\pi$ -A- $\pi$ " species **B13**, are unremarkable, indicating that the DOB moiety itself is not an inherently strong two-photon chromophore. However, when DOB acts as an acceptor in molecules with A- $\pi$ -A, A-D-A or D-A-D structural motifs,  $\eta\delta$  values can be very large indeed, consistent with the structure-property relationships described in section 4A, and with the DOB moiety acting as a strong acceptor in conjugated systems. In a short A- $\pi$ -A system such as **B1**, this enhancement is slight, but in the longer biphenyl- fluorene- and dihydrophenanthrene-bridged species (**B4-B7, B9**), the cross-sections are approximately an order of magnitude greater. Similarly, the  $\eta\delta$  values increase considerably when the basic structure of **B13** is decorated with alkoxy donors (**B14-B18**). Lengthening of the  $\pi$ -systems of these D-A-D molecules (**B19**) leads to even larger  $\eta\delta$ . Replacement of alkoxy groups with even stronger amine donors leads to a value for **B20** the order of  $10^{-47}$  cm<sup>4</sup>sphoton<sup>-1</sup>; one of the largest values reported in this energy range.

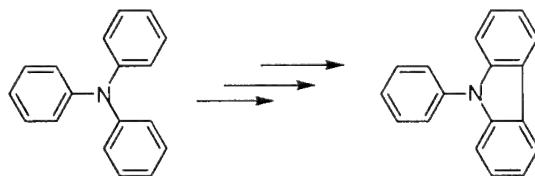
The large two-photon cross sections observed for some of these materials clearly indicate the potential for DOBs to act as optical limiters, and as components of two-photon photorefractives. A provisional patent has been submitted on these materials. Some of the DOB materials have been sent to Eric Van Stryland (Univ. of Central Florida) for optical limiting measurements. In addition, we have measured mobilities for some of the highly electron-deficient glassy dioxaborine derivatives. Time-of-flight measurements on one of these compounds gives an electron mobility of between  $10^{-3} - 10^{-2}$  cm<sup>2</sup>/V-sec, which is larger than any value reported in the literature for a glassy material by one to two orders of magnitude. However the behavior is highly dispersive and thus we still view this value with some significant degree of skepticism. Nonetheless, this result suggests that DOBs could potentially serve as charge-transport components of photorefractive polymer composites.

**Table B2.** Two-photon absorption maxima ( $\lambda_{\max}^{2h\nu}$ ) and the product of the fluorescence quantum yield and two-photon cross-sections,  $\eta\delta$ , for some DOBs (all in toluene or dichloromethane).

compound	$\lambda_{\max}^{2h\nu}$ / nm ( $\eta\delta / 10^{-50} \text{ cm}^4 \text{s photon}^{-1}$ )
<b>B1</b>	546 (24.5), 710 (0.087)
<b>B5</b>	588 (289), 700 (9.2)
<b>B6</b>	608 (315); shoulder at ~650 (160), 774 (12.1), shoulder at ~820 (7.5)
<b>B7</b>	612 (350), shoulder at ~660 (200)
<b>B9</b>	608 (257), shoulder at ~650 (126), 750 (14.6)
<b>B11</b>	585 (157), between 690-740 (>150), 840 (46)
<b>B12</b>	572 (87), >685 (>28)
<b>B13</b>	566 (19.4), ~690 (3.1)
<b>B14</b>	shoulder at 570 (47), 644 (279), 775 (13.9)
<b>B15</b>	614 (91), 708 (140), 834 (20)
<b>B16</b>	644 (236), 775 (13.7)
<b>B17</b>	575 (54), 676 (360), 823(30)
<b>B18</b>	642 (69), 750 (157), 892 (31),
<b>B19</b>	818 (525), 966 (154)
<b>B20</b>	980 (3800) [measurements may be complicated by photodecomposition]
<b>B22</b>	574 (43)

#### 4C. Carbazole dimers for optical-limiting and photorefractive applications

We have previously shown that bis(diaryl amino)biphenyl ("TPD") derivatives and other donor- $\pi$ -donor systems may be used as effective optical limiters in the visible; the mechanism for the optical limiting being two-photon absorption, followed by excited state absorption [Perry, J. W.; Barlow, S.; Ehrlich, J. E.; Heikal, A. A.; Hu, Z. Y.; Lee, I.-Y. S.; Mansour, K.; Marder, S. R.; Röckel, H.; Rumi, M.; Thayumanavan, S.; Wu, X. L. *Nonlinear Optics* **1999**, *21*, 225-243; Ehrlich, J. E.; Ananthavel, S. P.; Barlow, S.; Mansour, K.; Mohanalingam, K.; Marder, S. R.; Perry, J. W.; Rumi, M.; Thayumanavan, S. *Nonlinear Optics* **2001**, *27*, 121-131]. In addition to potential application as multi-photon optical limiting materials, these compounds also have potential as hole-transport materials for photorefractive and other devices (TPD-type molecules are commonly used in organic light-emitting diodes and TPD polymers can be used in photorefractories [see section D]). One mode of decomposition that has been observed for TPD derivatives is photo-oxidation; this process can cause two of the aryl groups to link, with the loss of two hydrogen atoms (as protons), leading to formation of carbazole units within the molecule (shown for a simple triarylamine in Figure C1). Since, in general, a triarylamine and arylcarbazole will have different redox potentials and optical properties this decomposition can lead to unfavorable impacts upon device behavior (e.g. decreases in hole mobility). One possible way to circumvent this problem is to begin with carbazole-based molecules in which this mode of decomposition is no longer possible. Hence, here we describe the synthesis of compounds in which aryl groups in TPD-derivatives are linked, i.e. those incorporating the carbazole moiety.



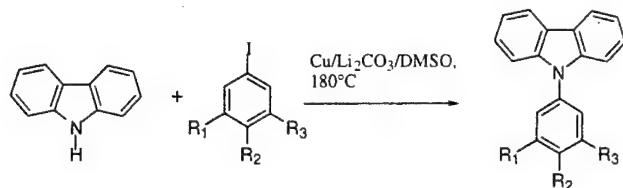
**Figure C1.** Photo-oxidation of triarylamines can lead to aryl carbazoles.

Schemes C1-C2 show the various steps of the synthesis of TPD-like carbazole dimers **C8-C14**. 9-Arylcarbazoles **C1-C7** were prepared in high yields from the Ullman coupling of carbazole and the corresponding iodo-aryl compounds (Scheme C1). These arylcarbazoles **C1-C7** were then dimerized using an oxidative coupling reaction, with  $\text{FeCl}_3$  in chloroform at room temperature as oxidant (Scheme C2). The resulting stable, deep-green-colored bicarbazolylium radical-cations were reduced to the neutral dimers **C8-C14** by methanol. For all reactions, the coupling always took place on the 3 position of carbazole ring. Although, in principle, coupling through the substituted phenyl ring is possible in the cases where  $R_2 = H$ , no such products were observed. The high selectivity of these coupling reactions is due to the role of the planarity of the carbazole moiety in stabilizing, through delocalization, the intermediate carbazole radical-cation.

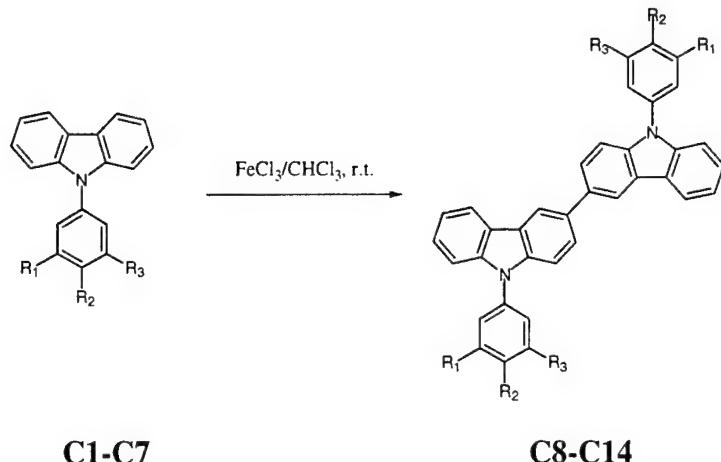
Glass-transition ( $T_g$ ) and melting temperatures ( $T_m$ ) of the carbazole dimers **C8-C14** were determined by differential scanning calorimetry (DSC) at a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$ . Table C1 summarizes the thermal properties of these species. On the first heating cycle all the compounds showed a melting endotherm. On cooling, stable glasses were formed, and on reheating the glass transitions were observed. Two of the compounds, **C9** and **C14**, were found to recrystallize exothermically subsequent to undergoing the glass transition, and then to melt at essentially the same temperature as observed on the first heating. Compared to the corresponding "TPD" compounds [Thayumanavan, S.; Barlow, S.; Marder, S. R. *Chem. Mater.* **1997**, 9, 3231-3236,  $T_g$ 's in range  $47\text{--}58\text{ }^{\circ}\text{C}$ ], the carbazole dimers exhibit considerably higher  $T_g$ 's, suggesting that glasses based on these materials are likely to be more stable with respect to recrystallization and phase segregation.

The substituents shown in the schemes were chosen to give a range of redox potentials for the carbazole dimers. The redox potentials were measured using cyclic voltammetry (CV) vs  $\text{AgCl}/\text{Ag}$  with a scan rate of  $50\text{ mV/s}$ . All carbazole dimers exhibited two one-electron reversible redox processes corresponding to successive reversions of mono- and

dications. The potentials for these two oxidation processes are listed in Table C2. The data clearly indicate that the HOMO energies of these materials can readily be tuned using substituent effects in a similar way to those of the analogous "TPD"s.

**Scheme C1****C1-C7**

<b>C1-C7</b>	<b>R<sub>1</sub></b>	<b>R<sub>2</sub></b>	<b>R<sub>3</sub></b>
<b>C1</b>	H	H	H
<b>C2</b>	H	Me	H
<b>C3</b>	H	OMe	H
<b>C4</b>	Me	H	H
<b>C5</b>	OMe	H	H
<b>C6</b>	F	H	H
<b>C7</b>	CF <sub>3</sub>	H	H

**Scheme C2**

<b>C8-C14</b>	<b>R1</b>	<b>R2</b>	<b>R3</b>
<b>C8</b>	H	H	H
<b>C9</b>	H	Me	H
<b>C10</b>	H	OMe	H
<b>C11</b>	Me	H	H
<b>C12</b>	OMe	H	H
<b>C13</b>	F	H	H
<b>C14</b>	CF <sub>3</sub>	H	H

---

**Table C1.** Melting ( $T_m$ ; from first heating), glass-transition ( $T_g$ ; from second heating), and crystallization ( $T_c$ ; second heating) temperatures for TPD-like carbazole dimers.

Compound	$T_m$ / °C	$T_g$ / °C	$T_c$ / °C
<b>C8</b>	205.2	94.7	
<b>C9</b>	212.6	94.1	171.6
<b>C10</b>	198.9	98.3	
<b>C11</b>	190.8	88.5	
<b>C12</b>	140.4	80.3	
<b>C13</b>	185.1	74.0	
<b>C14</b>	252.0	79.6	154.9

**Table C2.** Oxidation potentials of the carbazole species vs. AgCl / Ag.

compound	$\lambda_{\max}$ / nm	$^1E_{1/2}$	$^2E_{1/2}$
<b>C9</b>	323	+532	+807
<b>C10</b>	323	+515	+777
<b>C11</b>	323	+546	+825
<b>C12</b>	323	+567	+844
<b>C13</b>	323	+622	+896
<b>C14</b>	324	+656	+930

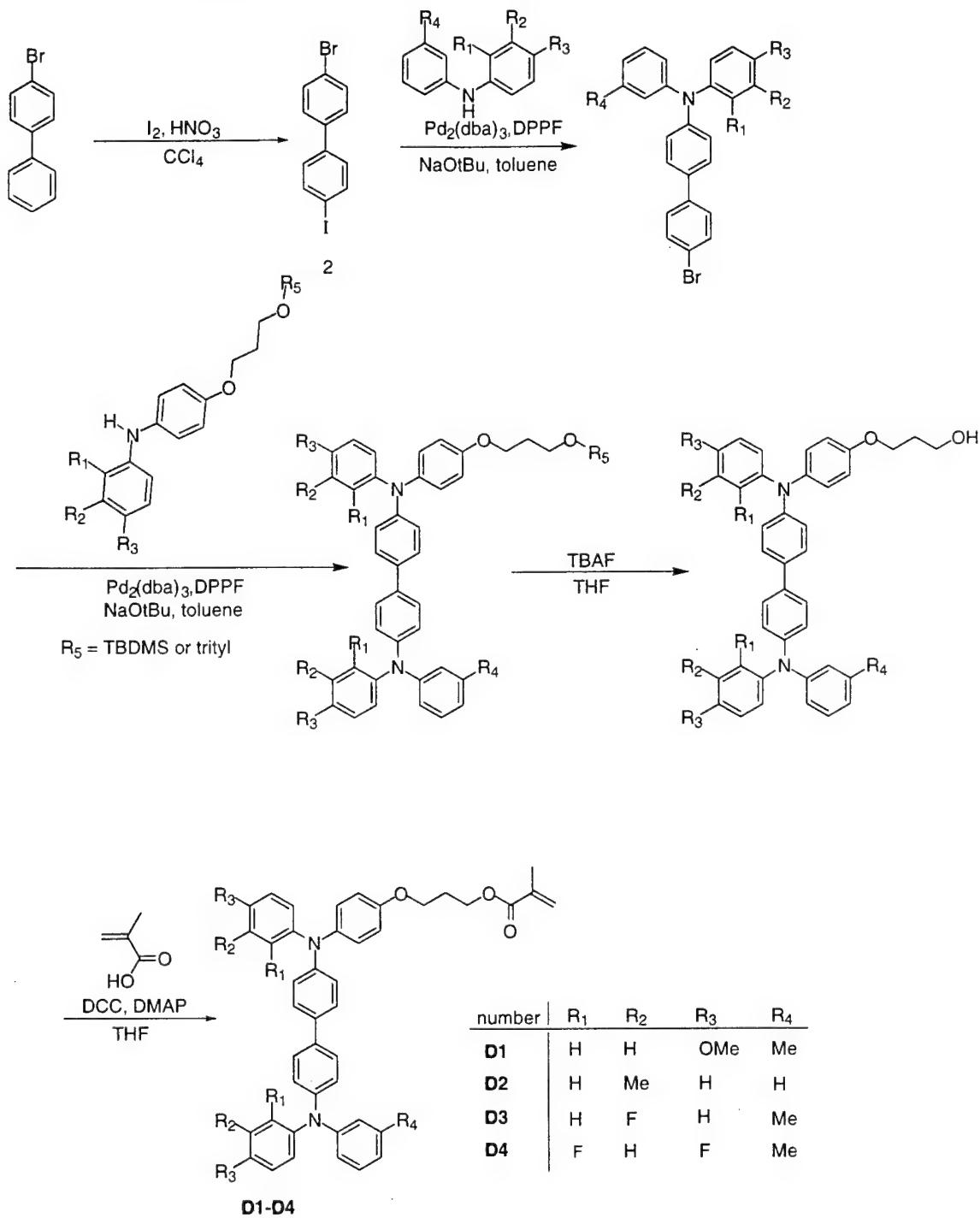
These new carbazole-based TPD-analogues are anticipated to have similar optical-limiting properties in the visible to the parent TPDs and to act as charge-transport agents for devices, such as in photorefractive polymer composites. As with the TPDs, it has been

possible that frontier energy levels of the molecules can readily be tuned for specific applications by variation of the substituents. However, the new compounds have higher glass-transition temperatures than their TPD equivalents, which will open up possibilities for more thermally stable devices, and are anticipated to show considerably enhanced photo-oxidative stability.

#### 4D. TPD polymers for optical-limiting and photorefractive applications

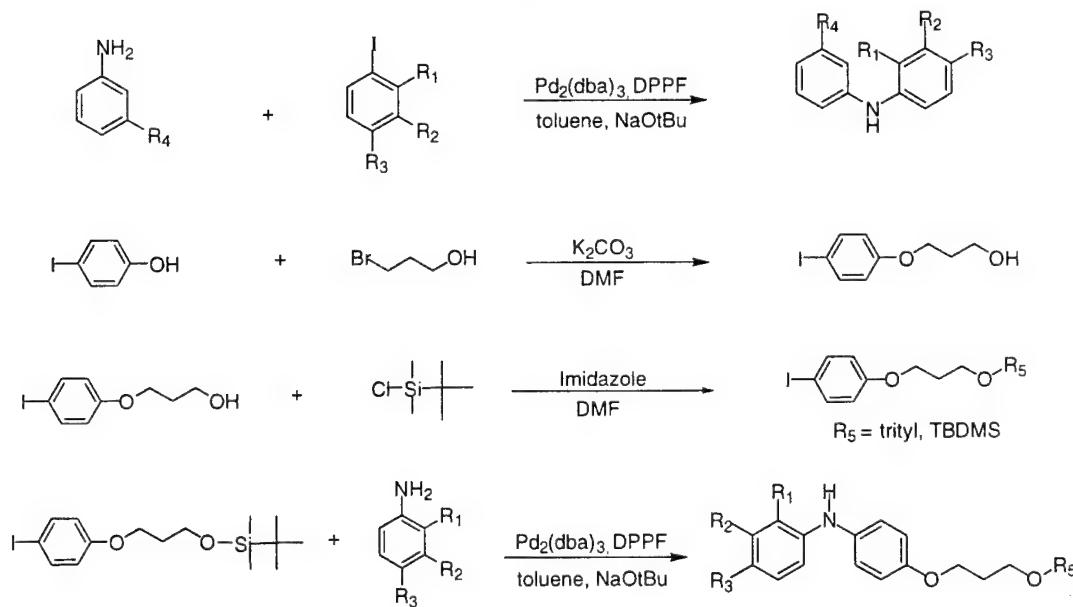
We have previously shown that bis(diaryl amino)biphenyls, so-called "TPD"s, are useful optical limiters in the visible [Perry, J. W.; Barlow, S.; Ehrlich, J. E.; Heikal, A. A.; Hu, Z. Y.; Lee, I.-Y. S.; Mansour, K.; Marder, S. R.; Röckel, H.; Rumi, M.; Thayumanavan, S.; Wu, X. L. *Nonlinear Optics* **1999**, *21*, 225-243; Ehrlich, J. E.; Ananthavel, S. P.; Barlow, S.; Mansour, K.; Mohanalingam, K.; Marder, S. R.; Perry, J. W.; Rumi, M.; Thayumanavan, S. *Nonlinear Optics* **2001**, *27*, 121-131]. In addition, the charge-transport ability of molecular TPDs is well known and they are frequently used as hole-transport agents in devices such as organic light-emitting diodes. TPD-based polymers are anticipated to have the optical and charge-transport properties of the molecular compounds, whilst being castable into thermally stable films. We have, therefore, synthesized some new polymers in which TPD moieties are functionalized with polymerizable acrylate groups. The substituents on the terminal aryl groups allow the redox potential of the polymers to be tuned.

The synthesis and molecular structures of the TPD methacrylate monomers is shown in Scheme D1. The strategy is based on the palladium-catalyzed C—N bond formation reaction developed by Buchwald and Hartwig, using the tris(dibenzylideneacetone)-dipalladium ( $Pd_2(dbu)_3$ )/1,1'-bis-(diphenylphosphino)ferrocene (DPPF) catalyst system in the presence of sodium *tert*-butoxide. An important feature is the selectivity shown for coupling an amine to the aryl iodide functionality, rather than the aryl bromide, of 4-bromo-4'-iodobiphenyl in the second reaction in the scheme.

**Scheme D1.** Synthesis of monomers **D1-D4**.

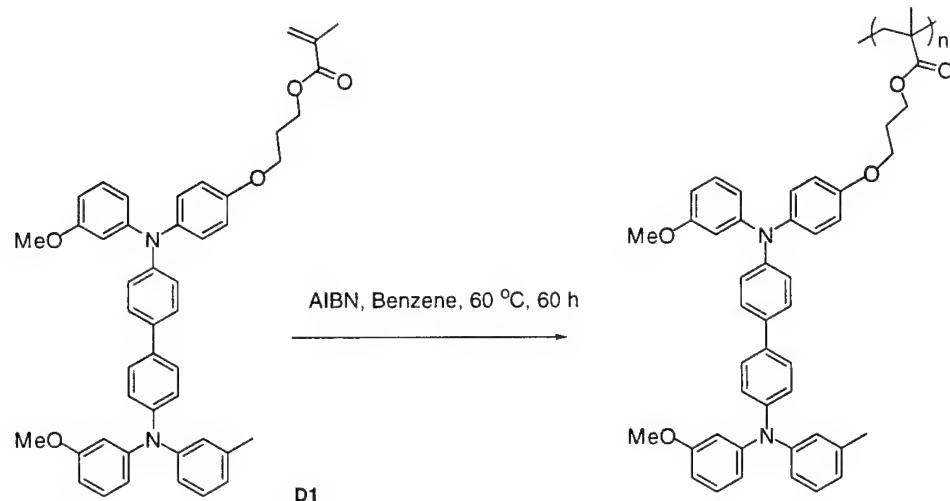
The monomers **D1** and **D2** were obtained in pure form after column chromatography on silica gel, eluting with a 7:3 mixture of dichloromethane:hexanes; monomer **D1** was purified by column chromatography on silica gel, eluting with dichloromethane. Pure monomer **D3** was obtained by re-precipitation of the crude product from tetrahydrofuran (THF) in methanol (purification on silica gel was initially avoided as similar compounds reportedly decompose on silica gel; however, this was not observed with compounds **D1**, **D2**, and **D4**). The secondary amines used in the second and third steps of Scheme D1 were also synthesized using palladium-catalyzed coupling reactions, as shown in Scheme D2. The hydroxy groups can be protected using either or *tert*-butyldimethylsilyl (TBDMS) protecting groups; the latter was found to be preferable due to the ease which it can be installed and removed.

**Scheme D2.** Synthesis of secondary amines used in the synthesis of TPD monomers shown in Scheme D1.



Monomer **D1** has been polymerized using 2,2'-azobis(isobutyronitrile) (AIBN) as an initiator under argon at 60 °C for 60 h (as shown in Scheme D3). The polymer was obtained in pure form as a white powder after precipitation three times, once from benzene into methanol and twice from THF into methanol. The structure of the polymer was confirmed by NMR spectroscopy and elemental analysis. The polymer was readily soluble in common organic solvents including THF, chloroform, toluene, benzene and dichloromethane. **D1** and the other monomers have also been copolymerized with other acrylates.

**Scheme D3.** Polymerization of **D1**.



The redox potentials of the monomers **D1-D4** were determined by cyclic voltammetry in dichloromethane and are reported in Table D1. The cyclic voltammograms show two sequential reversible one-electron processes corresponding to the successive removal of two electrons from the bis(diarylamo) biphenyl unit. The potentials are similar to the redox potentials of the corresponding non-polymerizable molecular compounds and to other TPD polymers; however, they are somewhat easier to oxidize due to the electron-donating nature of the ether linkage to the polymerizable group. The compounds demonstrate the expected

trend of increasing redox potential as the electron-donating substituents on the bis(diaryl amino)biphenyl moiety are replaced with electron-withdrawing substituents.

**Table D1.** Redox potentials of hole-transport monomers in  $\text{CH}_2\text{Cl}_2$  (values are reported relative to the ferrocenium/ferrocene couple).

Monomer	$^1\text{E}_{1/2}(\text{mV})$	$^2\text{E}_{1/2}(\text{mV})$
<b>D1</b>	105	360
<b>D2</b>	190	470
<b>D3</b>	300	540
<b>D4</b>	320	595

These polymers are anticipated to show high hole mobilities, which are currently being measured in collaboration with the Optical Sciences Center at the University of Arizona. Materials with high charge carrier mobilities are used in a variety of technologies, such as OLEDs, OFETs, photovoltaics and photorefractive polymers. Moreover, we have recently studied the photogeneration efficiencies of TPD and its derivatives in doped polystyrene, sensitized with  $\text{C}_{60}$ . At 633 nm, photogeneration values of 100% are obtained at applied electric fields as low as  $55 \text{ V}\mu\text{m}^{-1}$ . These results strongly suggest that TPD-polymers, such as those we describe here, will be useful in photorefractive applications. Indeed, we are currently working on photorefractive devices in which the polymer **C5** is the hole-transport agent. Moreover, these materials will also have good optical-limiting properties in the visible part of the spectrum.

**Participation at meetings, conferences, and seminars**

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### Honors and Awards

7/97 - 6/99	NSF Special Creativity Award Extension
2/95	3M Lecturer in Materials Science, University of British Columbia
9/93	Lew Allen Award for Research, The Jet Propulsion Laboratory
7/87 - 11/88	National Research Council Resident Research Associate The Jet Propulsion Laboratory

- 9/84 - 6/85      W.R. Grace and Company Industrial Fellowship  
                      University of Wisconsin at Madison
- 8/82                Departmental Commendation for Excellence in Teaching  
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- 6/77 - 8/77        National Science Foundation Summer Science Training Program in Chemistry  
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